

## PATENT ABSTRACTS OF JAPAN

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## (54) PRODUCTION OF CATALYST FOR PRODUCTION OF METHACRYLIC ACID

## (57)Abstract:

PURPOSE: To improve reaction activity, selectivity, catalyst strength and catalyst life by rapidly supplying a catalyst raw material soln. for production of this catalyst consisting of a partially neutralized salt of the heteropoly acid expressed by the prescribed formula mixing the soln. by high-speed stirring and subjecting the soln. to an aging treatment by heating under high-speed stirring.

CONSTITUTION: Production of this catalyst consisting of the neutralized salt of the heteropolyacid expressed by the formula is executed by preparing a molybdenum raw material soln. and a raw material soln. exclusive of this molybdenum raw material, rapidly supplying both solns. and subjecting the solns. to the aging treatment by heating in the presence of ammonia radicals, nitric acid radicals and sulfuric acid radicals under high-speed stirring. In the formula, P, Mo, V, As and O denote phosphorus, molybdenum, vanadium, arsenic and oxygen;

X denotes  $\geq 1$  kinds of the elements selected from a group consisting of rubidium, cesium and thallium; Y denotes  $\geq 1$  kinds of the elements selected from copper, silver, bismuth, iron, cobalt, antimony, lanthanum and cerium. Suffixes (a) to (g) are atomic ratios; (a), (c), (e) are  $\leq 3$  not inclusive of 0 when b=12, (d), (f) are  $\leq 3$  inclusive of 0 and (g) is a number exclusive of 0.

P: Mo: V: As: O: X: Y: 0.2

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**Notes:**

1. Untranslatable words are replaced with asterisks (\*\*\*\*).
2. Texts in the figures are not translated and shown as it is.

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**[Claim(s)]****[Claim 1]**

General formula  $\text{Pa Mob Vc Asd Xe Yf Og}$  (among a formula) P, Mo, V, As, and O express phosphorus, molybdenum, vanadium, arsenic, and oxygen, respectively. X expresses at least a kind of element chosen from the group which consists of rubidium, caesium, and thallium. When Y expresses at least a kind of element chosen from the group which consists of copper, silver, bismuth, iron, Cobalt, antimony, lanthanum, and cerium, and Subscript a, b, and c, d, e, f, and g express the atomic ratio of each element and it is referred to as  $b = 12$ , a, c, and e are three or less values which do not contain 0 (zero), and d and f are three or less values containing 0. the numerical value to which g becomes settled by the oxidation states and the atomic ratios of each element other than O -- it is -- [ the catalyst for methacrylic acid manufacture which consists of partial neutralizing salt of the heteropolyacid shown ] Use this catalyst component as at least two sorts of raw material solutions, and this raw material solution is mixed. Make an ammonium root and a nitric acid root, and/or a sulfuric acid root exist in mixed liquor, and precipitation of the Dawson type heteropolyacid salt which is a catalyst precursor is deposited. Heating aging treatment of the slurry solution obtained is carried out, concentration desiccation is carried out, in how to calcinate and manufacture in inert gas subsequently, a catalyst raw material solution is supplied quickly and churning mixing is carried out at high speed, And the manufacture method of the catalyst for methacrylic acid manufacture characterized by performing heating aging treatment under high-speed churning.

[Claim 2] The manufacture method of the catalyst for methacrylic acid manufacture according to claim 1 which carries out supply mixing of at least two sorts of catalyst raw material solutions within 8 minutes.

[Claim 3] The manufacture method of the catalyst for methacrylic acid manufacture according to claim 1 which it agitates [ agitate and the mixed time which is an index showing the mixed state mixes a catalyst raw material solution ] within 25sec using a churning mixing tub or a line mixer.

[Claim 4] The manufacture method of the catalyst for methacrylic acid manufacture according

to claim 1 that use a high velocity revolution shearing agitator, and a velocity gradient mixes and agitates a catalyst raw material solution by 3000-12000sec-1.

[Claim 5] The manufacture method of the catalyst for methacrylic acid manufacture according to claim 4 that a high velocity revolution shearing agitator is a gay mixer, a homogenizer, or a pipeline gay mixer.

[Claim 6] The manufacture method of the catalyst for methacrylic acid manufacture according to claim 1 which mixes a catalyst raw material solution using three or more static mixers with a number of elements.

[Claim 7] The manufacture method of the catalyst for methacrylic acid manufacture according to claim 1 that the mean particle diameter of the secondary grains of the Dawson type heteropolyacid salt which is the depositing catalyst precursor is 20micro or less.

[Claim 8] The manufacture method of the catalyst for methacrylic acid manufacture according to claim 1 of the mixed time which is an index showing the mixed state agitating heating aging treatment of a slurry solution within 25sec using a pressurization churning mixing tub, and performing it.

[Claim 9] The manufacture method of the catalyst for methacrylic acid manufacture according to claim 1 of performing heating aging treatment of a slurry solution at 100-200 degrees C.

[Claim 10] The manufacture method of the catalyst for methacrylic acid manufacture according to claim 1 that the amount of incorporation of V atom to the solid phase at the time of the end of heating aging treatment is [ V atom ] at least 0.2 to the Mo atom 12.

[Claim 11] The manufacture method of the catalyst for methacrylic acid manufacture according to claim 1 of performing calcination in inert gas at 400-500 degrees C.

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#### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to improvement of the catalyst for manufacture of the methacrylic acid by vapor phase catalytic oxidation reaction. It is related with improvement of the heteropolyacid system catalyst used in order to carry out gas phase catalytic oxidation of methacrolein, isobutane, isobutyric acid, the isobutyraldehyde, etc. with molecule-like oxygen in detail and to manufacture methacrylic acid.

[0002]

[Description of the Prior Art] Many catalysts for carrying out gas phase catalytic oxidation of the methacrolein, and manufacturing methacrylic acid are proposed, and the part is already used for production of a commercial scale (for example, a JP,50-101316,A number, a JP,50-142510,A number, a JP,59-4445,A number, etc.). Moreover, the catalyst for manufacture of the methacrylic acid by oxidation dehydrogenation (JP,57-72935,A number etc.) of isobutyric acid and oxidation (JP,57-144238,A number etc.) of isobutyraldehyde is also known well. Furthermore, the catalysts (JP,H2-42032,A etc.) for oxidizing the catalyst (JP,55-127328,A

number) for oxidizing isobutylene or the third class butanol, and manufacturing methacrylic acid and methacrolein and isobutane directly, and manufacturing methacrylic acid and methacrolein are proposed.

[0003] It is known that what has the structure of the heteropolyacid which all makes molybdenum and phosphorus a principal component, and/or its salt as a catalyst used for these reactions is effective, and be related with a presentation. Improvement of addition of cocatalyst components, such as partial displacement of molybdenum by \*\* vanadium, copper, antimony, and arsenic, etc. is proposed.

[0004] Various improvement, such as use of annular amine, is made also about the method of preparation. Carrying out under heating is known about the mixed conditions of the catalyst raw material, and carrying out above about 80 degrees C (JP,H4-7037,A, a JP,4-63139,A number, etc.) is proposed. Furthermore, after mixing using a line mixer, the method of preparation which carries out spray drying immediately is also known (JP,H4-182450,A).

[0005]

[Problem(s) to be Solved by the Invention] However, the problem of these catalysts known is that the point at which both reaction yield (activity and selectivity) and catalyst life are satisfied is not necessarily enough also in oxidation of the methacrolein already put in practical use. For example, compared with the catalyst which manufactures acrylic acid from acrolein, a lot of [ labile and a life / sufficiently therefore ] catalysts are needed not only the selectivity of a reaction is low, but, and the burden of the present condition of equipment cost and catalyst cost is large. It is one of the big Reasons that it does not have the enough performance of a catalyst the method of using isobutane, isobutyric acid, etc. as a raw material or that it cannot yet be industrialized, either.

[0006] This invention persons proposed that the catalyst which improves the above-mentioned purpose was acquired by preparing the slurry which uses a Dawson type heteropolyacid salt as a component as a catalyst precursor previously, and considering it as the catalyst of the Keggin type heteropolyacid by concentration-drying and calcinating (JP,4-63139,A number). It is in the technical problem of this invention improving this catalyst further, and offering the catalyst which doubles and has higher labile, selectivity, and catalyst hardness and a long catalyst life.

[0007]

[Means for Solving the Problem] In order to attain the above-mentioned technical problem, as a result of considering improvement of a heteropolyacid system catalyst wholeheartedly, this invention persons find out attaining the above-mentioned technical problem by improving the preparation processes of the Dawson type heteropolyacid salt which is a catalyst precursor, and came to complete this invention.

[0008] That is, this invention is general formula  $P_a M_o b V_c A_s d X_e Y_f O_g$  (among a formula). P, Mo, V, As, and O express phosphorus, molybdenum, vanadium, arsenic, and oxygen, respectively. X expresses at least a kind of element chosen from the group which consists of rubidium, caesium, and thallium. When Y expresses at least a kind of element chosen from the

group which consists of copper, silver, bismuth, iron, Cobalt, antimony, lanthanum, and cerium, and Subscript a, b, and c, d, e, f, and g express the atomic ratio of each element and it is referred to as  $b = 12/a, c, \text{ and } e$  are three or less values which do not contain 0 (zero), and d and f are three or less values containing 0. the numerical value to which g becomes settled by the oxidation states and the atomic ratios of each element other than O -- it is -- [ the catalyst for methacrylic acid manufacture which consists of partial neutralizing salt of the heteropolyacid shown ] Prepare this catalyst component in at least two sorts of raw material solutions, and this raw material solution is mixed. An ammonium root and a nitric acid root, and/or a sulfuric acid root are made to exist in mixed liquor, precipitation of the Dawson type heteropolyacid salt which is a catalyst precursor is deposited, heating aging treatment of the slurry solution obtained is carried out, concentration desiccation is carried out and a catalyst raw material solution is quickly supplied in how to calcinate and manufacture in inert gas subsequently, It is the manufacture method of the catalyst for methacrylic acid manufacture characterized by carrying out churning mixing at high speed, and performing heating aging treatment under high-speed churning.

[0009] Although the fundamental structure of the catalyst of this invention is the partial neutralizing salt by rubidium of the molybdophosphoric acid well known from the former, caesium, and thallium, vanadium and copper are further included as an essential ingredient. Arsenic is effective in improvement in methacrylic acid selectivity as other components, and adding for this purpose is recommended. Although that the catalyst containing these elements is effective is a place already known, the efficacy improves further by combining with the specific catalyst preparation conditions of this invention. It is possible to add elements, such as antimony, silver, copper, iron, Cobalt, lanthanum, and cerium, as an optional component in addition to the above-mentioned element.

[0010] In this invention, when carrying out heating aging treatment of the slurry solution which a catalyst raw material solution is mixed, and precipitation of the Dawson type heteropolyacid salt which is a catalyst precursor is deposited, and is obtained, it is indispensable to make an ammonium root and a nitric acid root, and/or a sulfuric acid root exist. These are made to usually exist by adding in a catalyst raw material solution as a catalyst raw material.

[0011] As a raw material, the following are usable. Although ammonium molybdate is suitable as a raw material of molybdenum and ammonium, you may use in combination with molybdenum oxide, molybdophosphoric acid, etc. ammonia, or ammonium salt. As vanadium, vanadium pentoxide, ammonium metavanadate, oxalic acid vanadyl, molybdo BANADO phosphoric acid, etc. can be used.

[0012] Although it is common to use phosphoric acid and arsenic acid as for phosphorus and arsenic, you may use them in the form of the salt of other essential elements, such as ammonium phosphate, etc. It is carried out by whether nitric acid root content compounds, such as whether as a raw material of a nitric acid root or a sulfuric acid root, either rubidium, caesium, thallium and an optional component are used as nitrate or sulfate, nitric acid, ammonium nitrate or sulfuric acid, and ammonium sulfate, are added. If a nitric acid root or a

sulfuric acid root exists in either of the raw materials, other rubidium, caesium, thallium, and optional components can also use a chloride, carbonate, a hydroxide, phosphate, etc.

[0013] The above-mentioned catalyst raw material is used as at least two sorts of aqueous solutions, or a suspension solution, mixes this solution, and deposits precipitation. If the Dawson type heteropolyacid salt which is a catalyst precursor does not deposit when preparing a catalyst raw material solution, it is not especially restricted what a catalyst raw material is mixed and it is considered as a raw material solution, but 2 of a molybdenum raw material solution and the raw material solution except a molybdenum raw material solutions are usually prepared. In addition, after it mixes other raw material solutions simultaneous as another solution about vanadium in addition to the raw material solution except a molybdenum raw material and the Dawson type heteropolyacid salt which is a catalyst precursor deposits, you may add.

[0014] The mixed conditions of these raw material solutions, i.e., a mixed temperature, a speed of supply, and the churning conditions at the time of mixing have great influence on catalyst performance.

[0015] a mixed temperature -- room temperature - it is good to mix [ 80-degree C ] at room temperature -50 degree C temperature preferably. It is more advantageous to act as both about mixing as soon as possible. That is, at least two sorts of catalyst raw material solutions which exist at a rate of the catalyst composition ratio are preferably supplied within 2 minutes still more preferably less than 5 minutes less than 8 minutes, and it is good to mix. It can add without adhering to this time about V component.

[0016] [ when performing catalyst preparation on a scale of being industrial, it is difficult to perform supply of a lot of liquid, and mixing at once for a short time with the batch process which adds the catalyst raw material solution of another side to one catalyst raw material solution, but ] In this case, a catalyst raw material solution may be divided, it may supply and mix in a small-quantity [ every ] short time, and you may double later, and may carry out by pouring simultaneously two sorts of catalyst raw material solutions continuously by a specified flow rate. If catalyst raw material solutions other than V atom are uniformly supplied and mixed at a rate of the composition ratio and precipitation is generated, it can carry out satisfactorily.

[0017] It is good to carry out as much as possible also about churning at high speed. It is carried out using the what is called tub type churning mixing tub specifically used generally, a line mixer, a static mixer, the high velocity revolution shearing agitator further named generically by the gay mixer, the homogenizer, a pipeline gay mixer, etc., etc. The high velocity revolution shearing agitator consists of the stators or screens which were formed in the turbine or the rotor, and its periphery part of the special form which carries out a high velocity revolution by separating clearance of 2mm or less from a rotation part. It is churning by mechanical energies produced between the turbine (rotor) and stator (screen) which carry out a high velocity revolution by 1-40m/sec \*\*\*\*\*, such as shearing force, pressure fluctuation, a cavitation, and collision power. As a high velocity revolution shearing agitator, a T.K gay mixer, a T.K pipeline gay mixer (made by special opportunity-ized industrial incorporated company),

Models, such as the Clare mix (made by M Technique Co., Ltd.) poly thoron homogenizer (KINEMATICA) and the Supra ton (made by Tsukishima Kikai Co. Ltd.), are mentioned. The form in particular of an agitator and churning wings etc. is not limited, and especially if high-speed churning can be performed, it will not be limited.

[0018] As an index showing a churning state, there is usually a churning power requirement per unit volume. However, when [ with same churning power requirement ] the existence of viscosity change and a baffle differs from the form of churning wings but, the mixed state may differ. [ since a remarkable clay change is caused during aging of slurry of a catalyst precursor in this invention, it is difficult to express a churning state with a churning power requirement correctly, but ] The churning business power immediately after a deposit of precipitation of the Dawson type heteropolyacid salt which is a catalyst precursor in a churning mixing tub is about 0.1 Kw/m<sup>3</sup>. They are about 0.25 Kw/m<sup>3</sup> preferably above. They are about 0.5 Kw/m<sup>3</sup> more preferably above. It is carried out above.

[0019] As an index with which a churning state is expressed in this invention, [ a churning mixing tub or a line mixer ] The mixed time which is time until complete mixing is attained [sec] (a definition is a chemical engineering manual refer to edition [ fifth ] the 896 pages), [ and a gay mixer etc. ] In used high velocity revolution shearing churning, a velocity gradient [sec<sup>-1</sup>] (definition full an id - mixing technology (Fluid Mixing Technology), 24page (1983), and McGraw-Hill Publication publication reference) is used.

[0020] In this invention, when a churning mixing tub or a line mixer is used, mixed time performs churning of less than about 5 to 10sec preferably about three to 25 sec. Although the shorter one of mixed time is desirable, it is difficult to realize about 3 or less sec, and since the energy more than needed is required, it is meaningless in practice. the case where a high velocity revolution shearing agitator is used -- a velocity gradient -- about 3000 -12000sec<sup>-1</sup> -- desirable -- about 5000 -10000sec<sup>-1</sup> is agitated. Since the energy more than needed is required, it is meaningless to carry out exceeding abbreviation 12000sec<sup>-1</sup> in practice. Moreover, also when a static mixer is used, it is necessary to consider it as the equipment which has churning performance equivalent to the above, and it is necessary to use the static mixer more than the number of 3 elements in this case.

[0021] As for the mean particle diameter of the secondary grains of the depositing Dawson type heteropolyacid salt, thing of about 20micro or less is obtained by such churning. Since the secondary particle diameter of the depositing Dawson type heteropolyacid salt becomes large even if the speed of supply of a catalyst raw material solution is slow, and the churning velocity at the time of mixing is slow, it has a bad influence on the heating aging treatment performed to the next, and catalyst performance falls. In addition, although the measured value of a grain size changes with pretreatments etc., in this invention, it is the value which agitated at least 5 minutes or more at 300rpm or more by the magnetic stirrer, made the sample what distributed slurry, using water as a solvent, and measured this with centrifugation-type particle-size-distribution measuring apparatus.

[0022] One or more hr heating aging treatment of the obtained slurry is carried out at about

100-200 degrees C after mixing. When heating aging treatment is about 100 degrees C or less, the invert ratio to methacrylic acid will become a low catalyst. Moreover, about [ being ineffective as for about 200 degrees C or more ] and heating aging treatment equipment will become expensive. The role of heating aging treatment is that change the presentation distribution between grinding of secondary grains, a deposit of each catalyst component atom in slurry, and re-elution, i.e., deposit grains (solid phase) and the liquid phase, and this catalyst makes it the suitable solid phase for this reaction, and slurry with a liquid phase presentation. The mean particle diameter of secondary grains is set to about 4micro or less by this heating aging treatment.

[0023] When a grain of 20micro or more deposits by mixed deposit in the mean particle diameter of secondary grains, grinding of grains does not take place easily due to heating aging, therefore change of the presentation distribution between the solid phase in slurry and the liquid phase does not take place easily. Change of the presentation distribution between the solid phase in slurry and the liquid phase is remarkable in especially V atom. In the case of this catalyst, how V atom is incorporated into solid phase is the factor which influences catalyst performance. Although it depends for the amount of incorporation of V atom to solid phase also on V brewing presentation, to the Mo atom 12, it is desirable that 0.2 or more V atoms are full at the end time of heating aging treatment for solid phase at least, and this is attained by the method of this invention.

[0024] Especially if there is heating aging processing time by about 1 or more hr, it will not be restricted, but it is usually about 1 to 50 hours. There is no effect beyond this of balancing it even if it carries out time treatment. Although it carries out agitating heating aging treatment with pressurization churning mixing vessels, such as the usual autoclave, the churning conditions in that case also have great influence on the performance of a catalyst. If a catalyst raw material solution is mixed also at the time of aging treatment and the Dawson type heteropolyacid salt which is a catalyst precursor is deposited, the same high-speed churning is required. In heating aging treatment, the viscosity of slurry improves as aging advances, since there is grinding of secondary grains. Therefore, unless it agitates at high speed, the temperature distribution in an aging tub and particle size distribution become uneven, and a high activity catalyst cannot be acquired with sufficient reproducibility. In addition, it is possible to process a mixed deposit of a catalyst raw material solution and heating aging treatment with the same reactor.

[0025] Concentration desiccation of the slurry which heating aging treatment finished is carried out with a well-known method, i.e., a compartment dryer, a drum dryer, a spray dryer, a band dryer, an infrared dryer, a pneumatic conveyor dryer, etc. The solid after desiccation serves as a Dawson type heteropolyacid salt. If this is heated at about about 150-350 degrees C, while transferring to a Keggin type heteropolyacid salt, neutralization products, such as ammonium nitrate which lives together, are removed. Although the process of this heating is carried out with well-known equipment, in order to avoid the bad influence to the catalytic activity and hardness by rapid decomposition of ammonium nitrate, it is desirable to heat the



heteropolyacid salt of form divided into about 10mm or less over several hours.

[0026] The heteropolyacid obtained in this stage serves as mixed salt with ammonium and X components (rubidium etc.), and the way things stand, there is no character of solid acid, and since activity is low, it is calcinated and activated. About 400-500 degrees C of calcination is preferably calcinated at the temperature of about 420-450 degrees C among inert gas atmosphere, such as nitrogen. Almost all ammonium components \*\*\*\* by this, it becomes proton acid, and high activity is discovered. When it calcinates in the air, in order that disassembly of a heteropolyacid and sintering may start above about 400 degrees C, activity may become low and many ammonium roots may remain below about 400 degrees C, activity is low too. After calcinating in the air with a temperature of about 400 degrees C or less, you may perform about 400-500 degrees C in inert gas atmosphere. After calcinating in inert gas, calcinating below about 400 degrees C in the air does not interfere. If it calcinates below about 400 degrees C in the air rather, selectivity will improve.

[0027] Although the catalyst of this invention begins oxidation of methacrolein and is used for manufacture of the methacrylic acid by oxidation of various raw materials In use, it is used for low surface area carriers, such as catalyst independence or alpha alumina, silica, and silicon carbide, in support or the form which carried out dilution mixing, and is fabricated and used for cylindrical, a globular shape, the shape of a ring, the shape of a clover, the shape of a gear, and massive \*\*. Although reaction form in particular is not restricted and a fixed bed, a fluid bed, a moving bed, etc. are used, catalyst form is suitably chosen by reaction form.

[0028] Methods, such as a molding method with a well-known method for fabricating in such form, i.e., tableting shaping, rolling granulation, extrusion, fluidized bed granulation, and spraying granulation, are used. You may add various kinds of additives, such as graphite, stearin acid, and glass fiber, at the time of shaping for improvement of moldability or the activity of a Plastic solid, and the improvement in hardness.

[0029] As for the physical properties of the catalyst acquired by this invention, generally, the thin volume after about 1 - 20 m<sup>2</sup> / g, and shaping of surface area is [ /g and the pore radius of about 500-10000Å and collapse hardness ] 1kg or more about 0.1-0.4cm<sup>3</sup>.

[0030] When catalytic oxidation of the methacrolein is carried out by a gaseous phase and methacrylic acid is manufactured using the catalyst of this invention, It is not necessary to be necessarily pure methacrolein as a raw material used, and what evaporated the methacrolein obtained with the liquid phase process also by the methacrolein content gas by which gas phase catalytic oxidation may have been carried out in isobutylene or tertiary butanol may be used. Although pure oxygen is sufficient as an oxygen source, air is used industrially. Nitrogen, carbon dioxide, a steam, etc. can be used as other dilution gas.

[0031] As for the ratio [ as opposed to about 1 to 10% and methacrolein in the methacrolein concentration in reaction material gas ] of oxygen, about one to about five are used. The space velocity of material gas is the range of abbreviation 500-5000h<sup>-1</sup>, and about about 260-340 degrees C of reaction temperature are desirable. As for reaction pressure, it is common to be carried out near ordinary pressure or under some pressurization.

[0032] Moreover, when oxidizing isobutane directly and manufacturing methacrylic acid and methacrolein using the catalyst of this invention, the high concentration of the isobutane concentration in material gas is better [ about 15% or more of ]. As an oxygen source, pure oxygen, oxygen enriched air, air, etc. are used.

[0033] About 0.2 to about two are suitable for the ratio of oxygen to isobutane. It is desirable to contain a steam in about 3 to 30% of range in reactant gas. Dilution gas, such as nitrogen, carbon dioxide, and carbon monoxide, may be contained in material gas. At this reaction, since an invert ratio is not made so highly, unreacted isobutane and a case recover oxygen and it is recycled. Subraw methacrolein is recycled, or is led to another reactor, and oxidizes to methacrylic acid. About about 270-340 degrees C of space velocity are [ abbreviation 300-3000h<sup>-1</sup> and reaction temperature ] desirable. Reaction pressure is performed under ordinary pressure or pressurization.

[0034] The catalyst of this invention can be used also for the methacrylic acid manufacture by oxidation dehydrogenation of isobutyric acid, and oxidation of isobutyraldehyde. Moreover, it is possible to use, also when manufacturing methacrylic acid from isobutylene in one step. At these reactions, the same reaction conditions as oxidation of methacrolein are employable.

[0035]

[Effect of the Invention] The catalyst acquired by the method of this invention has labile higher than the conventional catalyst, selectivity, and good hardness and a long catalyst life in manufacture of methacrylic acid. Since especially labile and selectivity are high, the industrial meaning is very large.

[0036]

[Example] This invention is not limited by these examples, although an example is given to below and this invention is explained still more concretely. The definition of an invert ratio and selectivity is as follows.

Invert ratio = [(reaction methacrolein mol number) / (supply methacrolein mol number)] x 100  
 selectivity = [(generation METAKURI acid mol number) / (reaction methacrolein mol number)] x 100  
 churning business power (it calculates by Nagata's formula) shows the value in the hypoviscosity in early stages of churning mixing (20cp).

[0037] 450g of phosphoric acid, phosphoric acid copper Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> 3H<sub>2</sub>O 130g, nitric acid caesium 819g, and 284g of 60% arsenic acid aqueous solutions were added to 4800g of example 1 ion exchange water 85%, it held at 40 degrees C, the churning dissolution was carried out, and it was considered as the uniform aqueous solution (A liquid is called). 6990g of ion exchange water is taught to the churning mixing tub with a product made from stainless steel 20L jacket (diameter 260mmphi, circular) which has the agitator which attached two-step paddle wings. Temperature was held at 40 degrees C. Ammonium molybdate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>32</sub>.4H<sub>2</sub>O] 6356g was added there, the churning dissolution was carried out, and it was considered as the aqueous solution (B liquid is called).

[0038] After having carried out churning velocity of two-step paddle wings under churning, having carried out whole-quantity pouring of the A liquid in 2 minutes at 150rpm (15.7sec of

mixed time, and churning business power 0.12 Kw/m<sup>3</sup>), depositing precipitation and considering it as slurry, 137g of vanadium pentoxides were added. In addition, when the particle size distribution of the grains at the time of a precipitation deposit was measured with centrifugation-type particle-size-distribution measuring apparatus, the mean particle diameter of secondary grains was 15micro.

[0039] When steam was poured in the jacket under churning, churning velocity was heated at 125 degrees C at 200rpm (11.8sec of mixed time, and churning business power 0.28 Kw/m<sup>3</sup>). and aging treatment was performed for 42 hours, it became slurry whose mean particle diameter of viscosity 4740cp and secondary grains is 2.6micro. The amounts of incorporation of V atom to slurry solid phase were 0.22 atoms to the Mo atom 12. The obtained slurry was moved to Butt and moisture was evaporated in the dryer at 120 degrees C. The hardening-by-drying thing of this stage was what is called Dawson type heteropolyacid structure as a result of the X diffraction.

[0040] 30 copies of water and four copies of glass fiber were added to 100 copies of hardening-by-drying things ground with the mortar, extrusion was carried out after kneading using the metal pattern, the shaping catalyst raw material 5mm in diameter and about 7mm in length was obtained, and this was calcinated at 435 degrees C in nitrogen-gas-atmosphere mind after desiccation at 120 degrees C. The catalyst of this stage was Keggin type heteropolyacid structure as a result of an X diffraction and infrared absorption analysis. This was further calcinated at 390 degrees C in the air, and the catalyst was acquired. In addition, the presentation of this catalyst removes the glass fiber component and oxygen atom which were added for shaping, and is P1.5 Mo12V0.5 As0.4 Cu0.3 Cs1.4. It is.

[0041] The glass reaction pipe with an inside diameter of 15mm was filled up with 9ml of this catalyst, 12mol of oxygen%, 16mol of steam%, the reaction pipe was performed by space velocity (STP basis) 670h<sup>-1</sup>, and the remainder did the activity examination for the material gas of the presentation which consists of nitrogen with through and the reaction temperature of 290 degrees C methacrolein 4 mol%. As a result, they were 90.5% of a methacrolein invert ratio, 83.7% of methacrylic acid selectivity, and 75.8% of a methacrylic acid yield.

[0042] In comparative example 1 example 1, B liquid was dropped using another churning mixing tub (44.4sec of mixed time, and churning business power 0.03 Kw/m<sup>3</sup>), having covered A liquid for 30 minutes, and the slurry which has a secondary grain with a mean particle diameter of 25micro was obtained. Except this, the catalyst was prepared like the example 1 and the activity examination was done. However, even if this slurry performed the same heating aging treatment as an example 1, viscosity did not improve at all. Moreover, there were few amounts of incorporation of V atom to slurry solid phase to the Mo atom 12 as 0.17. They were 93.8% of a methacrolein invert ratio, 79.1% of methacrylic acid selectivity, and 73.7% of a methacrylic acid yield as a result of the activity examination.

[0043] Set in the comparative example 2 example 1. The churning velocity of the two-step paddle wings of a churning mixing tub with 20L jacket containing B liquid was set as 75rpm (31.3sec of mixed time, and churning business power 0.02 Kw/m<sup>3</sup>), whole-quantity pouring of

the A liquid was carried out in 2 minutes under churning, and the slurry which has a secondary grain with a mean particle diameter of 40micro was obtained. Except this, the catalyst was prepared like the example 1 and the activity examination was done. The amount of incorporation of V atom to the slurry solid phase at the time of the end of aging was 0.19 to the Mo atom 12. They were 89.9% of a methacrolein invert ratio, 82.4% of methacrylic acid selectivity, and 74.1% of a methacrylic acid yield as a result of the activity examination.

[0044] Set in the example 2 example 1. The churning velocity of the two-step paddle wings of a churning mixing tub with 20L jacket containing B liquid was set as 250rpm (9.4sec of mixed time, and churning business power 0.55 Kw/m<sup>3</sup>), whole-quantity pouring of the A liquid was carried out in 2 minutes under churning, and the slurry which has a secondary grain with a mean particle diameter of 7micro was obtained. Except this, the catalyst was prepared completely like the example 1 and the activity examination was done. The amount of incorporation of V atom to the slurry solid phase at the time of the end of aging was 0.28 to the Mo atom 12, and the mean particle diameter of secondary grains was 3.3micro. They were 91.8% of a methacrolein invert ratio, 83.9% of methacrylic acid selectivity, and 77.0% of a methacrylic acid yield as a result of the activity examination.

[0045] 450g of phosphoric acid, phosphoric acid copper  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  130g, nitric acid caesium 819g, and 284g of 60% arsenic acid aqueous solutions were added to 4800g of example 3 ion exchange water 85%, it held at 40 degrees C, dissolution churning was carried out, and it was considered as the uniform aqueous solution (A liquid is called). Ammonium molybdate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{32} \cdot 4\text{H}_2\text{O}]$  6356g was added to 6990g of ion exchange water held at 40 degrees C, the churning dissolution was carried out, and it was considered as the aqueous solution (B liquid is called). A liquid and B liquid were divided into ten, respectively, and it kept warm and saved at 40 degrees C.

[0046] The jacket of the separable flask with a glass 2L jacket which attached anchor wings was made to circulate through 50-degree C warm water, and it agitated at 200 morerpm. They are A liquid and B liquid there. \*\*\*\* in 2 minutes what was divided into ten, deposit precipitation (12sec of mixed time, and churning business power 0.26 Kw/m<sup>3</sup>), and it is considered as slurry. After continuing churning for 2 more minutes, the operation transported to the churning mixing tub with a product made from stainless steel 20L jacket which has the agitator which attached two-step paddle wings was repeated 10 times. Then, 137g of vanadium pentoxides were added, it fabricated [ it heating-aging-processed / of an example 1 and this appearance /, it dried and ] and calcinated, the catalyst was prepared, and the activity examination was done. The amount of incorporation of V atom to the slurry solid phase at the time of the end of aging was 0.22 to the Mo atom 12. They were 94.0% of a methacrolein invert ratio, 80.7% of methacrylic acid selectivity, and 75.9% of a methacrylic acid yield as a result of the activity examination.

[0047] It is the same operation as example 4 example 3, and they are A liquid and B liquid. Using a feed pump for the gay mixer (the model M made from special opportunity-ized Industry) which is rotating at 5000rpm after preparing, as for A liquid, 185 ml/min and B liquid

are 304 ml/min. It \*\*\*\*(ed), precipitation was deposited and slurry was generated. The velocity gradient of this high velocity revolution shearing churning was 7850sec<sup>-1</sup>. After slurry stagnated for 20 seconds within the gay mixer, it was transported to the churning mixing tub with a product made from stainless steel 20L jacket which has the agitator which attached two-step paddle wings. After ending the above-mentioned operation in 30 minutes, 137g of vanadium pentoxides were added, it fabricated [ it heating-aging-processed / of an example 1 and this appearance /, it dried, and ] and calcinated, the catalyst was prepared, and the activity examination was done. The amount of incorporation of V atom to the slurry solid phase at the time of the end of aging was 0.21 to the Mo atom 12. They were 91.2% of a methacrolein invert ratio, 84.9% of methacrylic acid selectivity, and 77.4% of a methacrylic acid yield as a result of the activity examination.

[0048] Although deposited precipitation by the same operation as comparative example 3 example 4, slurry was prepared, vanadium pentoxide was added and heating aging was performed, The churning velocity at the time of heating aging was reduced to 75rpm (31.3sec of mixed time, and churning business power 0.02 Kw/m<sup>3</sup>) from 200rpm (they are 0.28 Kw/m<sup>3</sup> with 11.8sec of mixed time, and churning business power), and heating aging treatment was started. Although slurry viscosity improved and 1100cp(s) were reached 5 hours afterward from the aging start back, the temperature in a tub (125 degrees C) began to fall, and the temperature in viscosity 2800cp and a tub fell to 108 degrees C in 21 hours after an aging start. then, slurry is taken out and it is the same as that of an example 1 -- it dried, fabricated and calcinated, the catalyst was prepared and the activity examination was done. The amount of incorporation of V atom to the slurry solid phase at the time of the end of aging was 0.19 to the Mo atom 12. They were 91.0% of a methacrolein invert ratio, 81.2% of methacrylic acid selectivity, and 73.9% of a methacrylic acid yield as a result of the activity examination.

[0049] Using the product made from stainless steel 100 l. churning mixing tub with a jacket which has the agitator (with [ of four sheets ] a baffle) which attached the two-step paddle wings of the example 5 length-of-a-wing ratio (ratio of the diameter of a vane to a tank diameter) 0.5, it was operated like the example 1 on the 5 time scale of the example 1, and the catalyst was prepared. At that time, the churning velocity at the time of a precipitate deposit and heating aging was 130rpm (21.1sec of mixed time, and churning power requirement 0.27 Kw/m<sup>3</sup>), the mean particle diameter of the secondary grains at the time of the end of aging was 3.0, and the amount of incorporation of V atom to slurry solid phase was 0.24 to the Mo atom 12. They were 92.6% of a methacrolein invert ratio, 83.9% of methacrylic acid selectivity, and 77.7% of a methacrylic acid yield as a result of the same activity examination as an example 1.

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